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(54) RECOVERY OF NICKEL FROM NICKEL SULFATE
SOLUTIONS

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Abstract of the Disclosure

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A process for recovering nickel, cobalt and similar metals from aqueous solutions wherein they are present as sulfates by introducing hydrogen sulfide into the solution while at a pH of about 2.5 to about 3.5, maintaining the pH of the solution in said range by introducing a calciferous base into said solution concurrently with the hydrogen sulfide, recovering the precipitated material from said solution and separating said precipitated material into a calcium sulfate rich fraction and a metal sulfide rich fraction by flotation.

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The present invention is concerned with separation and recovery of metals as sulfides from aqueous sulfate solutions and, more particularly, the separation and recovery of such metal sulfides at the lowest possible cost.

As those skilled in the art are well aware, it is conventional to precipitate various metals out of aqueous solution using hydrogen sulfide as a reagent. It is known that as hydrogen sulfide is added and metal precipitates as a sulfide, the hydrogen ion concentration of the solution tends to increase. In copending Canadian application Ser. No. 151,413 assigned to a common assignee with this application (said Canadian application corresponding to U.S. application Serial No. 381,861) it is disclosed that readily filterable sulfide precipitates of nickel, cobalt, zinc etc. can be produced by maintaining the pH of the solution within a critical narrow range at the outset and during the addition of hydrogen sulfide. There is a caution in this application that when dealing with sulfate solutions pH maintenance must not be accomplished using calcium-containing reagents. As to prior art suggestions, reference is made to German patent No. 720,881 of May 18, 1942 wherein there is disclosed a process wherein a calciferous base is initially added to a sulfate solution containing nickel, zinc or cadmium, hydrogen sulfide is passed through the solution mix to precipitate the metal as sulfide and flotation is used to separate the precipitated mixture.

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The difficulty with the aforementioned prior art is that copending Canadian application Serial No. 151,413 did not recognize the utility of any calciferous base in association with sulfate solutions and taught instead the use of much more expensive neutralizing reagents. One obviously

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cannot employ expensive reagents on a large scale to recover metals, especially relatively low value metals, without seriously jeopardizing the economics of the whole metal recovery scheme. The German patent suggestion is not commercially operative, because, as demonstrated hereinafter by comparative tests, the degree of separation of the precipitated products is low resulting in highly contaminated metal sulfide and significant metal sulfide loss in the flotation tailings.

10 It has not been discovered that by a special combination of carefully controlled process operations highly satisfactory recoveries of metal sulfide can be achieved from aqueous sulfate process solutions using the cheapest possible reagents.

It is an object of the present invention to provide a novel process for the recovery and separation of sulfides of nickel, cobalt, zinc and other similar metals from aqueous sulfate solutions.

20 Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention contemplates a process for recovering metal sulfides from aqueous sulfate solutions containing metal ion from the group of nickel, cobalt, zinc and copper, which comprises concurrently introducing H₂S and a calciferous base in stoichiometrically equivalent amounts into said solution while maintaining the pH within the range of about 2.5 to about 3.5 to precipitate the metal sulfide and to form a solid calcium sulfate phase essentially free of sulfide and thereafter froth floating said slurried precipitate to separate the metal sulfide from the calcium sulfate (gypsum).

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For the purposes of the present specification and claims the term "calciferous base" includes the basic compounds lime (CaO), slaked lime (Ca(OH)₂) and limestone or calcium carbonate (CaCO₃) as well as mixtures and intermediates thereof and natural products rich in said basic compounds.

For purposes of economy ground limestone, the cheapest of the calciferous bases is preferred for use in the process of the present invention. Also for purposes of this specification and claims the term "froth floating" includes all processes involving

- 10 the formation of a froth and the collection on air bubbles of said froth of sulfide particles. While froth floating has been described hereinbefore as involving a slurry containing a frothing agent and a sulphydryl collector and having a pH in a specially designated range those skilled in the art will appreciate that other collectors can be equivalent for the intended purpose and that other materials and other conditions can be used in the slurry for well known purposes.

Although the present invention is broadly applicable to the precipitation of all the metals mentioned hereinbefore as sulfides, the subsequent particular description will be set forth in terms of nickel recovery.

Speaking more particularly, an appropriate feed solution entering the process of the present invention is an aqueous sulfate nickel solution containing about 5 to about 50 grams per liter (gpl) of nickel. Such a solution can readily be obtained by oxidative treatment of nickel sulfide ores, the sulfate ion of the solution being ultimately derived from the sulfur of the sulfide ore. If the solution contains suspended solids other than calcium sulfate, it is advantageously clarified or filtered.

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The nickel-containing solution is now ready to enter the reaction zone wherein sulfide precipitation occurs. The reaction can be carried out as a batch process, or more advantageously as a continuous process using flow of nickel ion counter-current to hydrogen sulfide and calcium carbonate.

As indicated hereinbefore the acid and basic reagents are added in a stoichiometrically equivalent amounts so as to maintain the pH of the reaction medium in the range of 2.5 to 3.5. The addition of the H₂S (acid reagent) and calcium carbonate (basic reagent) can be controlled and monitored by means of a conventional recording pH meter coupled to signal feed back means to control the reagent feeding mechanisms.

10 The sulfide precipitation can be carried out at any temperature within the range of about 40°C to about 80°C and, while neither necessary nor practical, pressures higher than atmospheric can be used. In batch operations complete precipitation of nickel as the sulfide can be detected by a redox electrode system. However, in the most advantageous aspect of the invention, i.e., precipitation in a series of reactors involving counter-current flow of metal ion versus precipitation and neutralization agents a redox-electrode system is not operable and is unnecessary.

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After sulfide precipitation is complete, the barren solution plus precipitate may be thickened or filtered. The barren solution usually contains a maximum of about 50 parts per million (ppm) of nickel. The thickener underflow is removed as a flotation slurry containing about 10 to about 30% of solids by (weight). At this point flotation reagents in conventional amounts are added to the slurry. Specifically

30 a sulphydryl collector such as potassium amyl xanthate in

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amounts of about 0.05 to about 0.5 gram per kilogram (gm/kg) of solids (e.g., 0.25 gm/kg) and a frother such Dow SA.1263 frother in an amount of about 0.1 to about 5.0 gm/kg of solids (e.g., 0.15 gm/kg) can be used. As well known to those of ordinary skill in the art, any other of the soluble xanthates, e.g., potassium ethyl xanthate, sodium isopropyl xanthate etc., or mixtures thereof can be used as collectors. Many other frothers are available, for example Aerofroth 65, Barrett oil, cresylic acid, Dowfroth methyl amyl alcohol, methyl isobutyl 10 carbinol which can be used. In addition to the frother and collector, the flotation slurry can contain small amounts of activators, depressants, etc., the functions of which are well known to those of ordinary skill in the art and are described in texts such as Froth Flotation, D.W. Fuerstenau, Editor, 50th Anniversary Volume, The American Institute of Mining, Metallurgical and Petroleum Engineers Inc. New York 1962.

The froth flotation operation of the present invention can be carried out in any suitable flotation device or machine. Generally satisfactory results can be readily obtained in a 20 conventional subaeration machine having a rougher stage and a cleaner stage. All test results set forth in this specification were obtained using subaeration type machines for laboratory and pilot scale work. In both cases, tails, essentially nickel-free, and concentrate, essentially gypsum-free, are produced.

In order to give those skilled in the art a better understanding and appreciation of the invention all details

~~DEFINITION OF THE INVENTION, THE FOLLOWING~~
Examples are given -

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TABLE II

Batch Precipitation Conditions

Initial Ni Conc'n, gpl	pH	Temp	Time	Barren Solution Assay, gpl	Flot. pH	Flotation Results			% Distribution Ni	% Distribution Ca
						Wt. %	%Ni	%Ca		
7	2.5	75°C	32 min	0.089	2.6	Cl. Conc Tails	45.8 4.2 50.0	61.5 0.25 0.14	0.6 29.0 39.0	99.7 0.1 0.2
5.6	2.5	75°C	30 min	0.0055	2.6	Conc Tails	44.5 55.4	54.8 0.21	3.4 24.0	99.5 0.5
48.6	2.5	75°C	50 min	0.0072	2.5	Conc Tails	35.6 64.4	59.4 0.16	1.24 23	99.5 0.5
6.8	2.6	55°C	30 min	0.140	2.6	Cl. Conc Tails	35.0 4.0	62.3 10.9	0.33 —	97.1 2.0
6.8	3.5	55°C	32 min	0.0034	3.5	Cl. Conc Tails	41.2 2.9	61.3 0.84	0.83 —	99.5 0.1
						Tails	55.9	0.19	—	0.4

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EXAMPLE III

Because of its obvious pertinence to the present invention a series of locked cycle tests was conducted comparing the procedure disclosed in German patent No. 720,881 with the process of the present invention. Basically, these tests consisted of dual series of batch precipitations of nickel sulfide according to both the German and presently disclosed procedures using calcium carbonate as the calciferous alkali and recycling a portion of the precipitate to seed the succeeding precipitation of the series. In flotation, using both a cleaner stage and a rougher stage, cleaner tails were recycled to the rougher stage. This type of batch flotation testing with recycle of intermediate products is referred to as "locked cycle". The test criteria and results from these comparative tests are set forth in Tables III(a) III(b) III(c) and III(d). Table III(a) sets forth the precipitation and flotation conditions for the test series.

TABLE III(a)

	Precipitation	German Pat. No. 720,881	Present Invention
20	Reactor Volume	3 liters	3 liters
	Temperature	58°C	55°C
	pH	5.0-2.5	3.0
	H ₂ S feed rate	500 ml/min.	500 ml/min
	Reaction Time	33 min.	36 min.
	Stirring Rate	1000 rpm	1000 rpm
	Recycle	0.5 liters	0.5 liters
Flotation			
30	Collector (Amyl xanthate)	0.5 gm/kg	0.5 gm/kg
	Frother (Dowfroth SA-1263)	0.3 gm/kg	0.3 gm/kg
	Conditioning Time	0.5 min.	0.5 min.
	Roughing Time	4-3/4 min.	2-1/2 min.
	Cleaning Time	4-1/2 min.	2 min.
	pH	2.5	3.0

Table III(b) sets forth a summary of conditions and results.

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TABLE III(b)

		German Pat. No. 720,851	Present Invention
	H ₂ S feed rate Temperature	500 ml/min 58°C	500 ml/min 55°C
Stoichiometric Equivalence Limestone /Ni		1.0	1.01
Barren Solution Assay		30 ppm	150 ppm
Tailings	(Wt. Dist'n (Ni Assay (Ni Dist'n	23.2 2.11 9.2	64.2 0.11 0.4
Concentrate	(Wt. Dist'n (Ni Assay (Ni Dist'n <td>76.8 29.2 97.9 45 55 31</br></td> <td>35.6 62.3 99.6 96 4 8.8</td>	76.8 29.2 97.9 45 55 	35.6 62.3 99.6 96 4 8.8
Separation efficiency *		20-55%	97.5%

Tables III(c) and III(d) set forth specific details of the results of the locked cycle flotation tests using the procedures of the German patent and the present invention respectively.

TABLE III(c)

German Patent No. 720,881

Test Concentrate	A	B	C	D	
Wt. Dist'n	66.8	82.8	73.0	84.5	
Ni Assay	41.0	25.2	27.1	23.6	
Ni Dist'n	98.3	97.8	97.1	98.4	
& NiS	63	39	42	36	
& Gypsum	37	61	58	64	
& Moisture (in filtered cake)	31	33	29	31	
<u>Tailings</u>					<u>D (Cleaner Tails)</u>
Wt. Dist'n	33.2	17.2	27.0	15.5	6.6
Ni Assay	1.46	2.69	2.21	2.09	2.40
Ni Dist'n	1.7	2.2	2.9	1.6	0.8
<u>Separation Efficiency %</u>	55%	22%	35%	20	
<u>Barren Liquor Assay (gpl)</u>	0.012	0.058	0.025	0.024	

* Separation Efficiency = Recovery of Ni in Cons. - Recovery of calcium in conc.

TABLE III(d)

Present Invention

<u>Test Concentrate</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Wt. Dist'n	37.1	35.2	35.5	35.6
Ni Assay	61.9	62.5	62.7	62.1
Ni Dist'n	99.7	99.7	99.5	99.5
% NiS	96	97	97	95
% Gypsum	4	3	3	5
% Moisture	13	7	7	8
10 (in filtered cake)				
<u>Tailings</u>				(D) (Cleaner Tails)
Wt. Dist'n	62.9	64.8	64.5	64.4
Ni Assay	0.10	0.11	0.17	0.15
Ni Dist'n	0.3	0.3	0.5	0.5
Separation Efficiency (%)	97%	98%	98%	97%
Barren Liquor Assay (gpl)	0.054	0.14	0.34	0.084

Tables III(a) through III(d) show that when using the procedure of the German patent not only are separation efficiencies poor to the point of commercial impracticality but also that concentrate filter cake moisture is high. On the contrary, using the procedure of the present invention excellent separation efficiencies are obtained and a relatively dry concentrate filter cake is provided as the product. Microscopic examination of the tailings from both processes show considerable sulfide intergrown with gypsum crystals in the tailings using the German procedure whereas the tailings from the process of the present invention are relatively free of this phenomenon.

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The following are further examples of the present invention using continuous precipitation and flotation techniques.

EXAMPLE IV

The feed liquor, containing 6-7 gpl nickel sulfate was preheated to a temperature of 50°C to 60°C and flowed into the first of three stirred 3 liter reactors at 200 milliliters per minute. Calcium carbonate in a 5% wt. slurry and H₂S were added simultaneously in such proportion that the pH was maintained between 2.5 and 3.5 in each reactor. The liquid cascaded from reactor to reactor with H₂S additions and limestone made in each reactor. The mean residence time of liquid was approximately 15 minutes in each reactor. The results of tests using the continuous precipitation apparatus are set forth in Table IV.

TABLE IV
RESULTS FOR CONTINUOUS NiS PRECIPITATION
IN THREE REACTORS

Total Residence Time (min)	pH of First Reactor	Temp	Feed Assay gpl Ni	%Ni Reacted* Reactor No.			Discharge Assay gpl Ni	
				1	2	3		
20	45	3.2	57°C	6.75	90.8	8.8	0.2	0.008
	45	3.1	57°C	6.85	88.3	5.6	4.9	0.082
	45	3.1	55°C	6.71	87.8	11.3	0.4	0.040
	45	3.0	54°C	6.30	97.0	1.8	0.5	0.0013
	45	3.1	55°C	7.08	93.7	5.8	0.4	0.0018
	45	2.9	54°C	6.8	92.6	6.2	1.0	0.005

* Based on feed to Reactor #1.

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Product from the third reactor was collected and then floated in locked cycle tests. The procedure was similar to that used for evaluating the German patent. The reactor discharge was divided into several batches. Each fraction was floated in rougher and cleaner stages with the cleaner tails recycled to the rougher stage (locked cycle). The results of these tests are set forth in Table V.

TABLE V

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LOCKED CYCLE FLOTATION OF CONTINUOUSLY PRECIPITATED NiS

Feed: pH 3.8, 0.008 gpl Ni

Test Concentrate	A	B	C	D	
Wt. Dist'n	22.9	21.7	21.8	20.2	
Ni Assay	64.0	64.1	64.1	64.1	
Ni Dist'n	99.4	99.45	99.55	99.66	
% NiS	98.9	99.0	99.0	99.0	
% Gypsum	1.1	1.0	1.0	1.0	
Tailings					Cleaner Tails
20 Wt. Dist'n	77.1	78.3	78.1	77.0	2.8
Ni Assay	0.12	0.10	0.08	0.041	0.41
Ni Dist'n	0.6	0.55	0.45	0.34	0.08

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In a second series of flotation tests, the nickel sulfide and gypsum product from the third continuous reactor flowed directly into the first cell of a continuous flotation unit. Flotation reagents, specifically amyl xanthate collector and Dowfroth SA-1263 frother were added in quantities of 0.5 gm/kg and 2-3 gm/kg solids. Aeration of the pulp yielded a froth portion containing mostly nickel sulfide and a tailing containing mostly gypsum. The results of several continuous flotation tests are given in Table VI.

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TABLE VI

RESULTS FOR CONTINUOUS FLOTATION OF CONTINUOUSLY
PRECIPITATED NiS

Conditions: 3% solids pulp density
 0.5 gm/kg Potassium Amyl Xanthate
 2.5 gm/kg Dowfroth SA-1263

	% Recovery	Concentrate	% NiS	% Gypsum	Tails	
		Grade, % Ni			% Loss	Grade, % Ni
10	99.3	55.7	86.1	13.9	0.7	0.16
	99.7	56.1	86.9	13.1	0.3	0.076
	98.2	56.7	87.7	12.3	1.8	0.34
	99.6	60.1	92.9	7.1	0.4	0.12
	99.4	55.0	85.0	15.0	0.6	0.16

In industrial practice, the reaction temperature of precipitation is advantageously about 50°C to about 75°C and a step would be added between the precipitation and flotation stages whereby the residual, dissolved H₂S in the pulp would be recovered and returned to the process. This is necessary to reduce reagent loss and also to eliminate dissipating a hazardous gas into the atmosphere. The H₂S recovery can be accomplished by drawing a vacuum on the pulp sufficient to ensure boiling. A pressure of 100 mm Hg was required to remove H₂S from a pulp at 50 to 60°C which resulted in recovery of a gas containing 85% H₂S and 15% water vapor.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for removing sulfides from an aqueous sulfate solution containing ion from the group consisting of nickel, cobalt, zinc and copper which comprises simultaneously introducing a calciferous base and hydrogen sulfide concurrently in stoichiometrical amounts into said aqueous solution to precipitate metal sulfide while maintaining a pH of about 2.5 to about 3.5 in said solution and to form a solid calcium sulfate phase essentially free of sulfide and thereafter froth floating the sulfide away from the calcium sulfate phase.
2. A process as in claim 1 wherein the precipitation is carried out at a temperature of about 40°C to about 80°C.
3. A process as in claim 1 wherein the metal ion in solution is nickel in an amount of about 5 to about 50 grams per liter.
4. A process as in claim 1 wherein the precipitation is carried out continuously in a series of vessels and aqueous solution of metal ion is flowed countercurrently to the hydrogen sulfide and calciferous base.
5. A process as in claim 4 wherein the precipitation is carried out at a temperature of about 50°C to about 75°C.
6. A process as in claim 1 wherein the calciferous base is limestone.
7. A process as in claim 1 wherein the froth flotation is carried out using a sulphydryl collector.
8. A process as in claim 1 wherein, between the precipitation and froth flotation steps, a step of degassing the barren solution is interposed.

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9. A process as in claim 8 wherein the degassing is by application of a partial vacuum to the solution and the collected hydrogen sulfide-rich gas is returned to the process.



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TABLE IB

Batch Precipitation Conditions

<u>Initial Conc.</u>	<u>pH</u>	<u>Temp.</u>	<u>Reaction Time</u>	<u>Barren Assay Ni</u>
15 gpl	4.0	75°C	75 min.	3.8 gpl
15 gpl	4.0	50°C	180 min.	1.6 gpl

Batch Flotation Conditions

Slurry from the foregoing were filtered, washed, repulped with fresh water then floated pH 6.5

10 Potassium amyl xanthate 0.12 g/kg
 Conditioning time 5 min.
 Flotation time 5 min.

Flotation Results

	Wt. %	Assay Wt. %		Distribution %	
		Ni	Ca	Ni	Ca
Conc	66.1	39.1	7.7	99.8	36.4
Tails	33.9	0.13	26.2	0.2	63.6
Conc	53.4	47.5	6.4	99.3	21.7
Tails	46.6	0.39	26.5	0.7	78.3

EXAMPLE II

20 The following series of tests was conducted with initial nickel solution concentrations of either about 7 gpl or 50 gpl, the pH of precipitation was between 2.5 and 3.5. The temperature was either 55°C or 75°C and the flotation was conducted directly on the precipitated pulp. The flotation reagent additions and flotation conditions were the same as before. Results are shown in Table II. It can be seen that excellent recoveries and separations were obtained under the conditions chosen.

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EXAMPLE I

Several samples of nickel-containing aqueous sulfate solution having a pH of 2.5 were treated with hydrogen sulfide and (calcium carbonate to maintain the pH) at 75°C to provide a precipitated product. The precipitated product was filtered and then slurried in water containing a frother and potassium amyl xanthate (dosage 0.06 gm/kg. of solids) conditioned for 5 minutes and froth floated for 5 minutes. The test conditions and results are set forth in Table 1A.

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TABLE 1A

Batch Precipitation Conditions

<u>Initial Conc</u>	<u>pH</u>	<u>Temp.</u>	<u>Reaction Time</u>	<u>Barren Assay Ni</u>
7 gpl	2.5	75°C	32 min.	81 ppm
7gpl	2.5	75°C	35 min.	37 ppm

Batch Flotation Conditions

Slurry from the foregoing were combined, filtered, washed, repulped with fresh water then floated at pH 6.5

20
Potassium amyl xanthate 0.12 g/kg
Conditioning time 5 min.
Flotation time 5 min.

Flotation Results

Conc.	Wt. %	<u>Assay Wt. %</u>		<u>Distribution, Wt. %</u>	
		Ni	Ca	Ni	Ca
Conc.	52.7	53.6	4.06	99.9	16
Tails	47.3	0.075	23.0	0.1	83

Other similar tests wherein the precipitation of sulfide was conducted at a pH of 4.0 and the flotation pH was 6.5 resulted in significantly more gypsum (calcium) being present in the concentrate as is shown in Table 1B.

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